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2b. DECLASSIFICATION / DOWNGRADING S	AUG 1 2 1988	Approved for public release;	
		distribution unlimited.	
4. PERFORMING ORGANIZATION REPORT NUI	WBER(S) H	5. MONITORING ORGANIZATION PEPORT NUMBER(S)	
		. ARD 23475.4-MS	
3. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
Colorado State University	( 577	U. S. Army Research Office	
c. ADDRESS (City, State, and ZIP Code)		7b. ADDRESS (City, State, and ZIP Code)	
Faut 0-11/ 00 00522		P. O. Box 12211	
Fort Collins, CO 80523		Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
U. S. Army Research Office		HRO-MIPR-136-87	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
P. O. Box 12211 Research Triangle Park, NC	27709-2211	PROGRAM PROJECT TASK WORK UNIT NO. NO. ACCESSION NO.	
11. TITLE (Include Security Classification) Semiconducting Transition Metal Silicides: New Materials for Optoelectronics on Silicon			
12 PERSONAL AUTHOR(S) Professor John E. Mahan			
13a. TYPE OF REPORT Final 13b. TIME COVERED 14. DATE OF REPORT (Year, Month, Day) 15. PAGE COUNT 5/31/87 5/31/88			
16 SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those			
of the author(s) and should not be construed as an official Department of the Army position,			
17. COSATI CODES	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD GROUP SUB-GROUP	<b></b> {		
Semiconducting transition metal silicide thin films of FeSi2, MnSi17, CrSi2, ReSi2, and IrSi1.75, were prepared. The electronic band structures were probed with measurements of the optical properties as a function of photon energy, together with measurements of the electrical resistivity as a function of temperature. The iron and manganese silicides possess direct forbidden energy gaps of 0.89 and 0.68 eV, respectively. The chromium and rhenium silicides exhibited apparently indirect gaps of slightly less than 0.35 and 0.12 eV, respectively. The bandgap of IrSi1.75 is close to that of silicon and could not be determined with the techniques available to us in this research. Applications for the semiconducting silicides, in optoelectronic chip interconnects and infrared detection, are noted.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT  DUNCLASSIFIED/UNLIMITED SAME AS RPT.  DOTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
		22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL	

# SEMICONDUCTING TRANSITION METAL SILICIDES: NEW MATERIALS FOR OPTOELECTRONICS ON SILICON

Final Report

Professor John E. Mahan

5/31/88

U.S. Army Research Office

ARD-MIPR-136-87

Contract or Grant Number: ARP 136 87(57 21)

Colorado State University Fort Collins, CO 80523

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### The Problem Studied

The purpose of this work was to examine the suitability of some semiconducting transition metal silicides as active optoelectronic device materials. These materials are IrSi<sub>1.75</sub>, FeSi<sub>2</sub>, MnSi<sub>1.7</sub>, CrSi<sub>2</sub>, LaSi<sub>2</sub>, and ReSi<sub>2</sub>. The motivation for the research was the ultimate desire to develop an optoelectronic device technology where both light sources and intrinsic semiconductor detectors may be monolithically integrated on a silicon chip.

The materials were prepared as thin films on silicon substrates. The silicide phases were formed by furnace reaction of sputter-deposited metal films with the substrates.

## Summary of Results

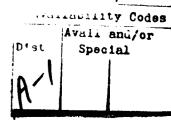
Since the last progress report we have completed our optical analysis of four semiconducting silicides. We will summarize our results for these materials now in order of increasing bandgap:

ReSi2 possesses an indirect bandgap of slightly less than 0.12 eV. The uncertainty is due to the fact that our measurements (of the phonon emission branch of the optical absorption constant) can only give us  $E_G + E_P$ , the bandgap plus the assisting phonon energy for the indirect transition. (The phonon absorption branch of the absorption spectrum was not experimentally accessible; if it were, then  $E_G$  and  $E_P$  could have been separately determined.) With typical phonon energies of a few hundredths of an electron volt, we can say that the bandgap is  $^{\sim}0.1$  eV. In addition, we observe a direct transition at 0.36 eV.

 $CrSi_2$  similarly possesses an indirect gap of slightly less than 0.35 eV and also exhibits an apparently direct transition at 0.67 eV. The uncertainty in bandgap value is due to the same reasons as for ReSi<sub>2</sub>.

 $MnSi_{1.7}$  displays a direct bandgap of 0.68 eV and there is evidence of





another direct transition at 0.82 eV.

Beta-FeSi<sub>2</sub> exhibits a direct gap of 0.89 eV. In these polycrystalline films we see extrinsic transitions at 0.38 and 0.14 eV, as well.

We find LaSi<sub>2</sub> to be a metal, rather than a semiconducting material as was indicated by our literature survey included in the proposal for this research. Metallic behavior was observed for both the low temperature tetragonal and high temperature orthorhombic phases. Their room temperature resistivities were found to be 24 and 57 micro-ohm-cm, respectively.

 $IrSi_{1.75}$  appears to possess a forbidden energy gap very near to that of silicon. This fact made it impossible for us to optically characterize the material in detail. Strong absorption by the silicon substrate obscured the optical properties of the silicide films.

We would like to note some potential technological applications of the first four materials for which results were summarized above. The two larger bandgap materials, by virtue of their direct bandgaps, may lend themselves to the creation of efficient solid state light sources. The direct gap is generally a requirement for efficient radiative recombination. Much work remains to be done, however, to achieve single crystal films and to investigate device physics. The bandgap values correspond to wavelength values (1.39 and 1.82 microns) that <u>may</u> be usable with silica-based optical fibers.

The two smaller bandgap materials probably will not lend themselves to the development of solid state light sources, because of their indirect gaps. However, their bandgap values correspond to wavelengths (~3.5 and 10.3 microns) of considerable interest for terrestrial infrared imaging, because , they lie within atmospheric transmission windows.

Finally, we would like to emphasize that, while we believe our analysis

of our polycrystalline films is solid, our results should be viewed with some caution until they are confirmed with measurements on, and analysis of, low defect density epitaxial films. In this regard, we are pleased to note that we have just received in our lab a new silicide MBE system manufactured by Perkin-Elmer. It is our desire to use this new growth system in the final year of the project (sponsored by the NSF) to make higher quality films for optical and photoelectronic characterization. The ARO will be advised of any additional results of significance and credited for any forthcoming publications.

#### Publications

- M.C. Bost and J.E. Mahan, "Semiconducting Silicides as Potential Materials for Electro-Optic VLSI Interconnects," J. Vac. Sci. Tech., B4(6), 1336 (1986).
- M.C. Bost and J.E. Mahan, "An Optical Determination of the Bandgap of the Most Silicon-Rich Manganese Silicide Phase," J. Electronic Materials, Vol. 16, No. 6, 389 (1987).
- M.C. Bost and J.E. Mahan, "An Investigation of the Optical Constants and Bandgap of Chromium Disilicide," J. Appl. Phys. <u>63</u> (3), 839 (1988).
- M.C.Bost and J.E. Mahan, "A Clarification of the Index of Refraction of Beta-Iron Disilicide," to appear in J. Appl. Phys.
- R.G. Long, M.C. Bost, and J.E. Mahan, "Optical and Electrical Properties of Semiconducting Rhenium Disilicide Thin Films," to appear in Thin Solid Films.
- R.G. Long, M.C. Bost, and J.E. Mahan, "The Metallic Behavior of Lanthanum Disilicide," submitted to Applied Physics Letters.

#### Conference Presentations

- M.C. Bost and J.E. Mahan, "Semiconducting Silicides: Potential Materials for Electro-optic VLSI Interconnects," Electronic Materials Conference, Amherst, MA (June 25-27, 1986).
- M.C. Bost and J.E. Mahan, "Semiconducting Silicides: Potential Materials for Electro-optic VLSI Interconnects," 4th Workshop on Refractory Metals and Silicides, San Juan Bautista, CA (May 12-15, 1986).
- Robert G. Long, M.C. Bost, and John E. Mahan, "ReSi2, a Narrow Bandgap Semiconductor," Workshop on Metals, Dielectrics, and Interfaces for VLSI, San

Juan Bautista, CA (May 9-12, 1988).

Robert G. Long, Melton C. Bost, and John E. Mahan, "Rhenium Disilicide: A Potential Material for Optoelectronic Integration," submitted to the 35th National Symposium of the American Vacuum Society.

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